Ultrasonic Observation of the Calcite–Aragonite Transition

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Abstract. Elastic-wave velocities were measured as a function of pressure by ultrasonic pulse interferometry in Solenhofen and Manlius limestone specimens to pressures of 27 and 38 kb. Longitudinal velocities decrease sharply from 5.3 km/sec at a mean pressure of 4 kb to a minimum of 4.8 km/sec at 8 kb. Transverse velocities decrease from 3.1 to 2.9 km/sec. At the minimum, bulk and rigidity moduli are 25 and 10 per cent below their 4-kb values. A density increase of 1.7 per cent is associated with this minimum. The observed effects are attributed to the calcite–aragonite transition, and they may be due to an inherent property of the material, a major component of which undergoes a polymorphic transition, the low- and high-pressure phases coexisting over a considerable pressure range. This may be an additional mechanism to account for low-velocity zones in the earth's interior.

Introduction. The phase diagram of $CaCO_3$ has been experimentally investigated by *Bridgman* [1939, 1947], *Jamieson* [1953, 1957], *Jamieson and Lawson* [1962], *G. J. F. MacDonald* [1956], *Clark* [1957], and *Adadurov et al.* [1961], using various techniques. *Bridgman* [1939], reporting pressure-volume data for Solenhofen limestone, white Vermont marble, and Iceland spar to 50 kb at room temperature found two transitions: $CaCO_3$ I–$CaCO_3$ II at 14.5 kb with a 0.4 per cent density increase; $CaCO_3$ II–$CaCO_3$ III at 17.8 kb with a 2.6 per cent density increase. Corresponding transitions in marble were observed at 10.8 and 21.6 kb by *Adadurov et al.* [1961] in similar experiments. The large compressibility observed by *Bridgman* [1939] in $CaCO_3$ II can be explained by the existence of still another transition (0.8 per cent density change at 15.7 kb) observed by *Adadurov et al.* [1961]. It is known that aragonite (2.95 g/cm^3) transforms to calcite (2.71 g/cm^3) when heated at atmospheric pressure. Since calcite has a higher entropy than aragonite [*Anderson*, 1934], the aragonite phase of $CaCO_3$ would be expected at sufficiently high pressure. However, *Bridgman* [1939] did not observe the calcite–aragonite transition up to 50 kb. The fact that aragonite may be precipitated in nature from aqueous solution at ordinary temperature and pressure [*MacDonald*, 1956] presents an additional problem.

Jamieson [1953] showed that aragonite was a high-pressure polymorph of calcite by measuring electrical conductivities of aqueous solutions of calcite and aragonite at different temperatures and pressures. He reported the transition at 3.8 kb at room temperature. *MacDonald* [1956] substantiated Jamieson's result using the 'simple squeezer' of *Griggs and Kennedy* [1956]. This work extended the calcite–aragonite transition line to 600°C and 13 kb by means of X-ray analysis of specimen disks rapidly quenched from a wide temperature and pressure range. *Clark* [1957] confirmed this result using a hydrostatic pressure cell and terminal X-ray analysis. Although *Jamieson's* [1957] X-ray result was not conclusive by itself, a thermodynamic argument indicated that both $CaCO_3$ II and $CaCO_3$ III were unstable with respect to aragonite.

Experimental method. A detailed description of the method of measurement appears elsewhere [*Ahrens and Katz*, 1962, called I below]. Briefly, a thin, disk-shaped specimen is compressed axially, while under lateral confinement by an annular pyrophyllite washer, in the geometry developed by *Bridgman* [1952]. An ultrasonic RF pulse, produced by quartz transducers which are mounted outside the stress field, is trans-

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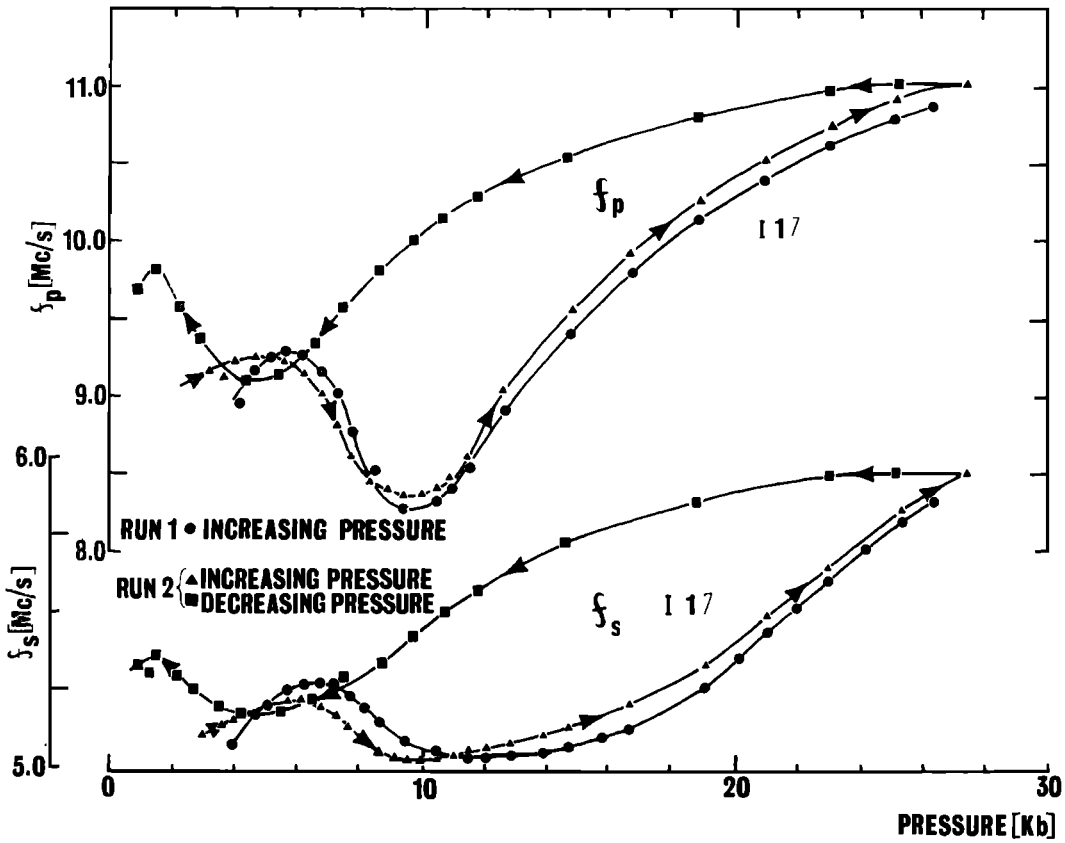

Fig. 1. Frequencies f_p and f_s versus pressure, Solenhofen limestone.

mitted through tungsten-carbide anvils into the specimen. The contrast in acoustic impedances between anvil and specimen produces a 180° phase shift between the signals reflected at the two anvil-specimen interfaces. This phase shift results in destructive interference for ultrasonic RF pulses, the carrier frequency of which is such that the specimen thickness is an integral number of half-wavelengths, provided that the pulse duration is long compared with the transit time. Measurement of these resonant frequencies for both longitudinal and transverse waves and of the initial specimen dimensions as a function of pressure permits calculation of the pressure derivative of the density. The latter may be integrated directly to give the specimen density and thickness. From these the elastic-wave velocities and constants are obtained. In the present experiment, the frequencies used were in the range 8 to 30 Mc/s. Specimen thicknesses were approximately 0.2 mm.

While the particular requirement of the present method with regard to specimen size, shape, and texture made it impossible to use calcite in the form of Iceland spar or marble, two limestones, Solenhofen[3] and Manlius,[4] were readily available and easily prepared into specimens of suitable shape. Solenhofen limestone has been studied in detail at lower pressure [*Birch and Dow*, 1936; *Birch and Bancroft*, 1938; *Birch*, 1942, 1960; *Hughes and Cross*, 1951]. To ensure that the observed pressure-dependence of elastic constants of the Solenhofen limestone was

[3] *Birch and Dow* [1936] list the following properties of Solenhofen limestone: density, 2.602 g/cm^3; $CaCO_3$, 96 per cent; balance, $MgCO_3$ and clay; diameter of calcite grains, 1–9 × 10^{-3} mm; porosity, approx. 0.6 per cent.

[4] R. Borst, Associate Curator, New York State Museum, has described the Manlius limestone specimen, collected at Ravena, New York, as an ostrocode pelsparite. It contains 99 per cent calcite with less than 1 per cent quartz and dolomite.

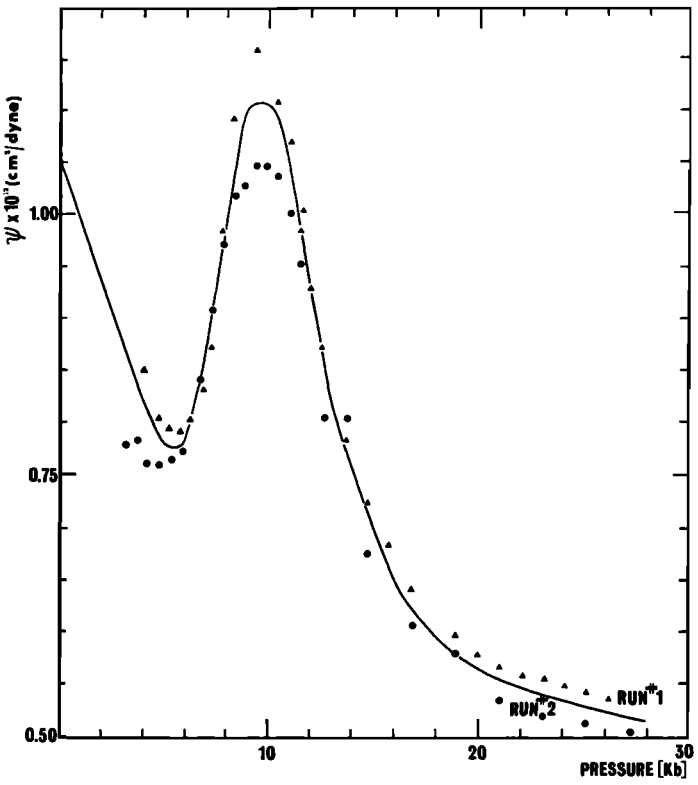

Fig. 2. Function ψ versus pressure, Solenhofen limestone, increasing pressure.

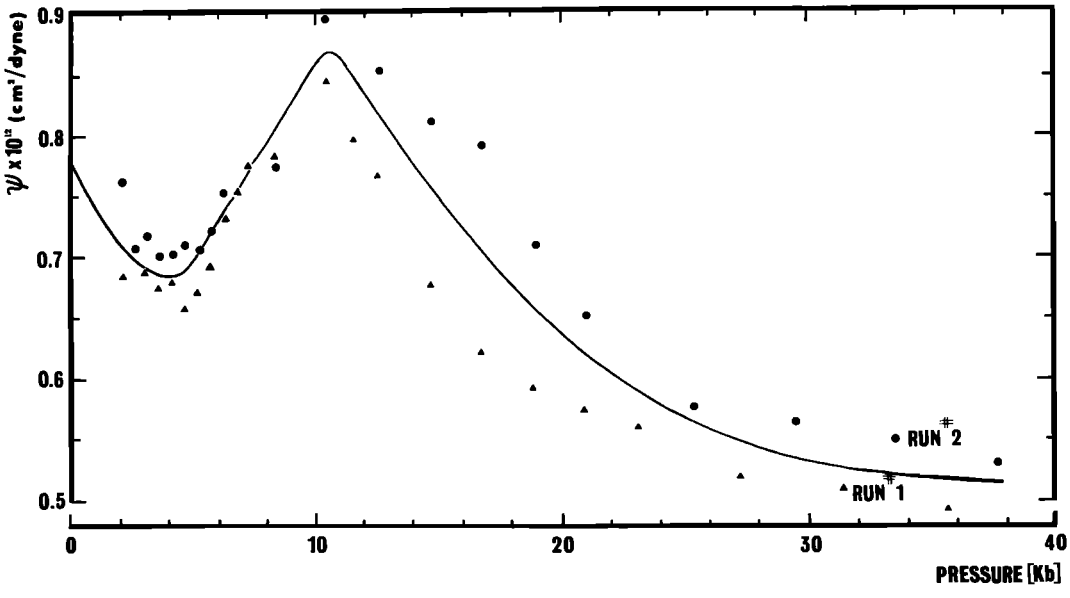

Fig. 3. Function ψ versus pressure, Manlius limestone, increasing pressure.

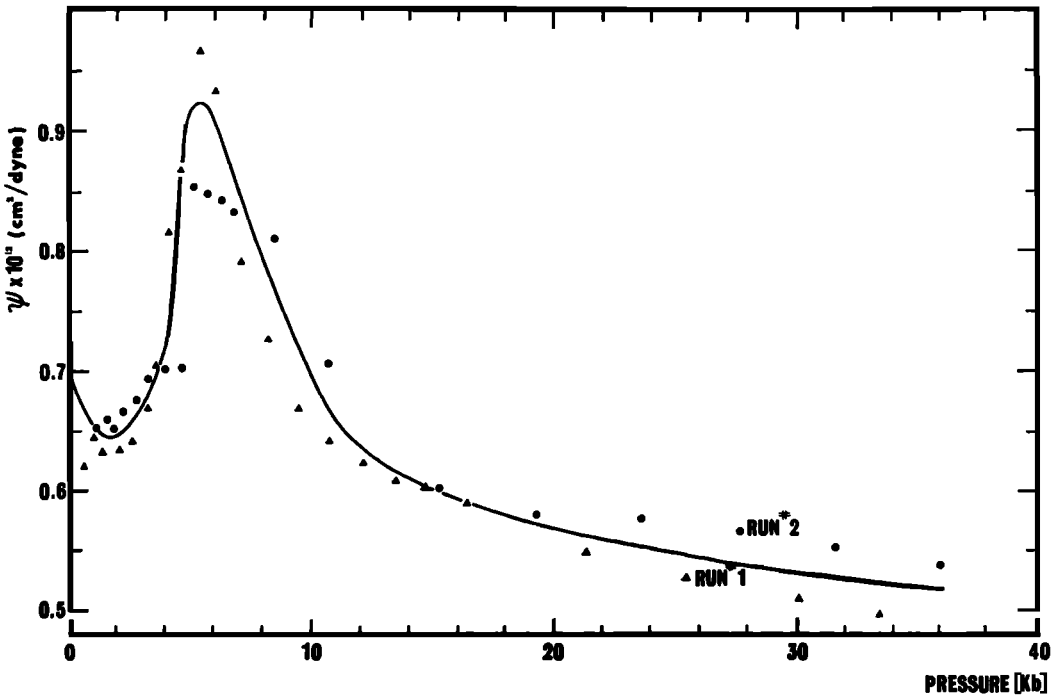

Fig. 4. Function ψ versus pressure, Manlius limestone, decreasing pressure.

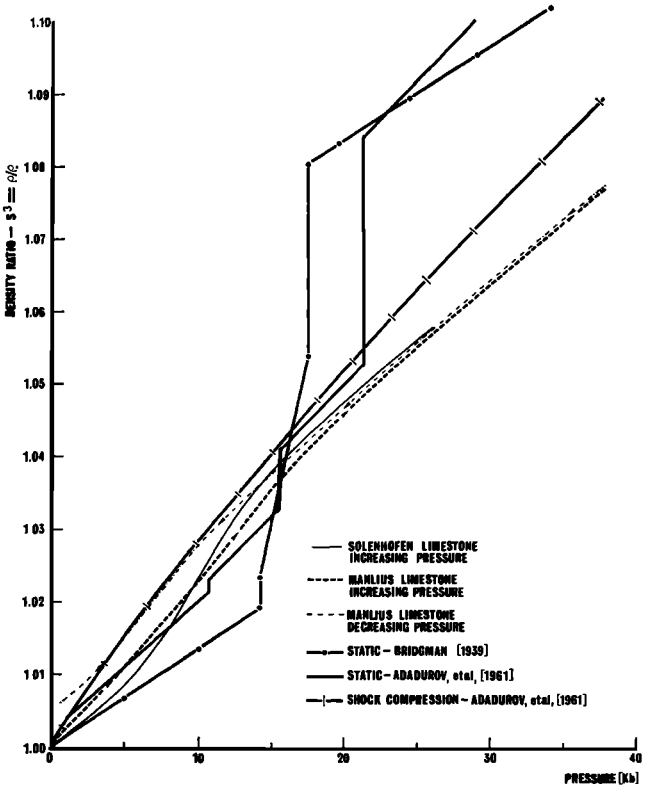

Fig. 5. Density versus pressure, Solenhofen and Manlius limestones.

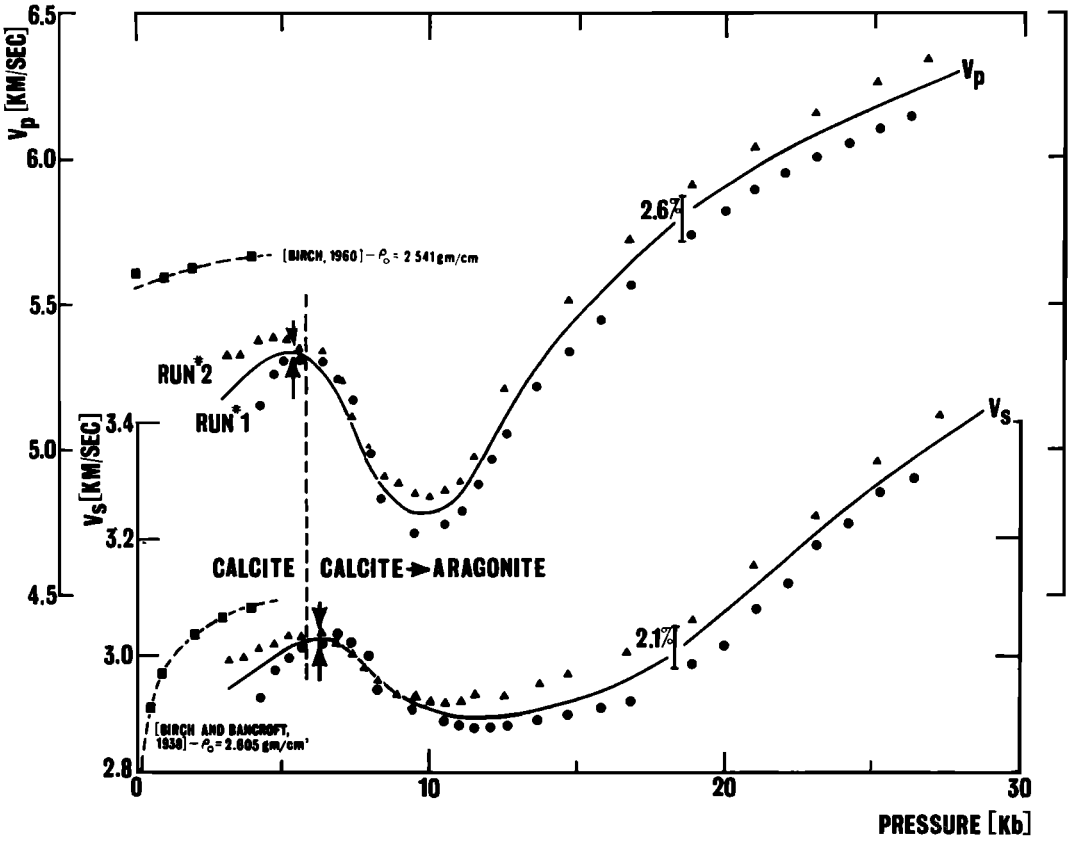

Fig. 6. Longitudinal and transverse velocities versus pressure, Solenhofen limestone, increasing pressure.

not a function of some unknown grain-size-dependent, mechanical process, the coarser-grained (0.5-mm) fossiliferous limestone Manlius was also studied.

Experimental results. The frequencies f_p and f_s, for which the specimen is a half-wavelength thick for longitudinal and transverse waves, decrease markedly in the 5- to 7-kb range during pressure application in the Solenhofen limestone (Figure 1). During pressure release the corresponding feature occurs at 1.5 kb. If $1 + \Delta$ is the ratio of adiabatic to isothermal bulk modulus,[5] l_0 and ρ_0 the initial thickness and density, and l and ρ the corresponding values at pressure P, the isothermal compressibility is (I)

$$1/K = 3l\psi/l_0 \qquad (1)$$

where

$$\psi = (1 + \Delta)/12l_0^2\rho_0(f_p^2 - 4f_s^2/3) \qquad (2)$$

Calculation of ψ (Figures 2, 3, 4) permits evaluation of specimen thickness and density from

$$l_0/l = (\rho/\rho_0)^{1/3} = 1 + \int_0^P \psi \, dP \qquad (3)$$

on the assumption of hydrostatic stress distribution in the specimen. The validity of this assumption can be tested by comparison of the results obtained with the present technique with those from hydrostatic loading arrangements (I).

From (1), the maximum in ψ (Figure 2) implies that the Solenhofen limestone specimens are very compressible in the 6- to 17-kb range. For the Manlius limestone, the corresponding range is 4 to 23 kb for increasing pressure

[5] For limestones, $\Delta \approx 0.006$, which is negligible compared with the experimental uncertainties of the quantities in the denominator of (2).

(Figure 3) and 1.5 to 16 kb for decreasing pressure (Figure 4). With $\rho_0 = 2.602$ g/cm³ for Solenhofen limestone, as given by *Birch and Dow* [1936], and 2.688 ± 0.003 g/cm³ for Manlius limestone, integration in (3) yields Figure 5, which indicates a 1.7 per cent density increase due only to the peak in the ψ functions. The uncertainty introduced by scatter in ψ (Figures 2, 3, 4) is ±0.5 per cent of the density. At 38 kb the density ratio is within 0.8 per cent of the value obtained by *Adadurov et al.* [1961] from shock compression of marble (Figure 5).

Elastic velocities follow from

$$v_p = 2lf_p \tag{4}$$

and

$$v_s = 2lf_s \tag{5}$$

Substitution of the numerical results from (3) into (4) and (5) gives the pressure variation of elastic velocities, for Solenhofen (Figure 6) and Manlius limestones (Figure 7) for increasing pressures and for Manlius limestone (Figure 8) for decreasing pressure. Values of longitudinal velocity obtained by *Birch* [1960] for 'lithographic limestone' and of transverse velocity [*Birch and Bancroft*, 1938] for Solenhofen limestone are also shown in Figure 6. A decrease in longitudinal velocity in Solenhofen limestone has been noted above 5 kb under hydrostatic conditions by Birch and Tozer (personal communication) and been attributed to the lower bulk modulus of aragonite as compared with calcite. Sources of experimental error include uncertainty in pressure, estimated as ±1.5 per cent near 20 kb from observation of the KCl transition (I) and the Bi I–Bi II transition (unpublished), and in initial specimen thickness (±1 per cent). Maximum estimated uncertainties in bulk and rigidity moduli and Poisson's ratio (Figure 9) from the scatter in velocities are ±8, ±3, and ±6 per cent, respectively. Values of bulk and rigidity moduli listed by *Birch* [1942] for Solenhofen limestone are also plotted in Figure 9.

The hysteresis observed in these measurements (Figures 1 to 4) is of the same magnitude as that observed by *Boyd and England* [1960] in which a solid pressure-medium apparatus was utilized.

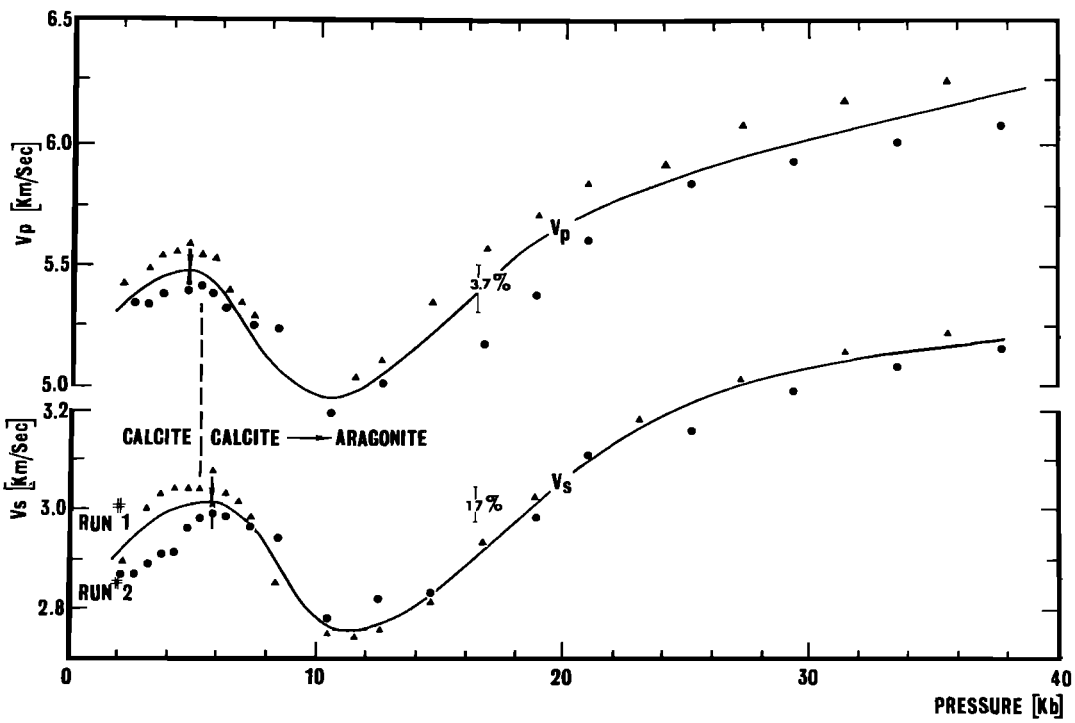

Fig. 7. Longitudinal and transverse velocities versus pressure, Manlius limestone, increasing pressure.

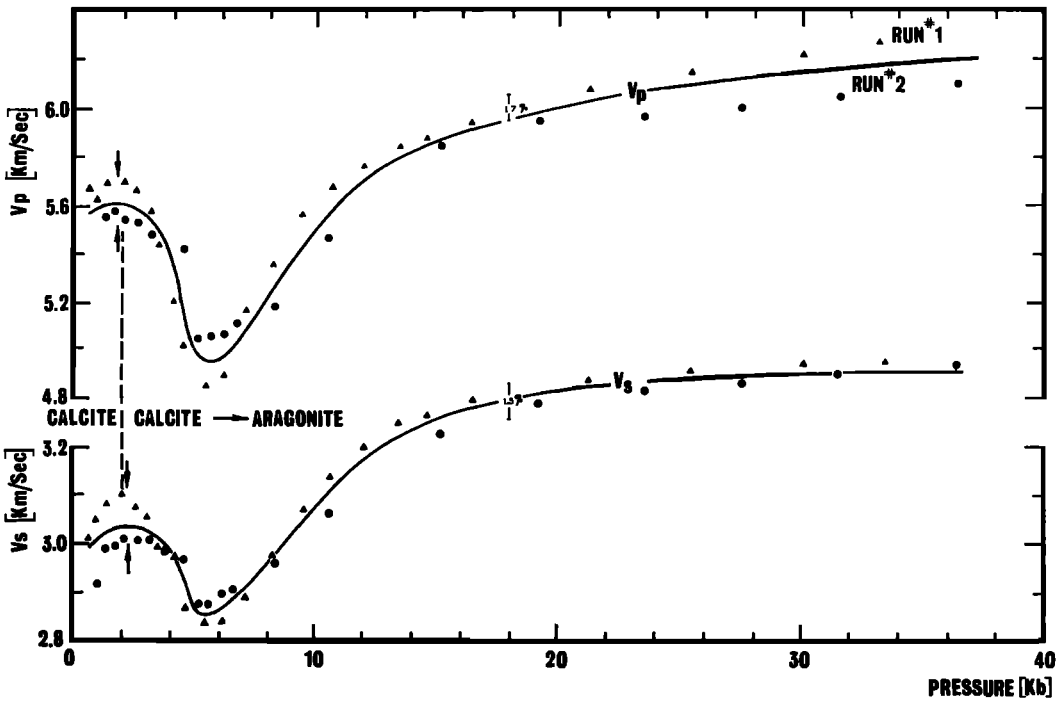

Fig. 8. Longitudinal and transverse velocities versus pressure, Manlius limestone, decreasing pressure.

Discussion. An abrupt pressure-volume transition would produce a change in slope of the f_p and f_s versus pressure curve and a sharp spike in the ψ versus pressure curve (I). In contrast, the observed pressure dependence of ψ and ρ (Figures 2 to 5) may be due (*a*) to time dependence of the volume transition; (*b*) to a radial pressure gradient across the specimen disk such that only the specimen's peripheral portion is above the transition pressure; and (*c*) to a volume transition in which the two polymorphs coexist over a range of pressure, independently of time, possibly caused by variation of stress from grain to grain within a polycrystalline material.

The first possibility was investigated by observing the effect of holding the pressure for long periods. Data accumulated over the course of several days were substantially identical with those obtained in a few hours. Perhaps greater periods are required to attain equilibrium than were available in these experiments. The second effect, although observed at higher pressures and under somewhat different conditions [*Montgomery et al.*, 1961], is considered unlikely to be important here, since it would not produce an intimate mixture of the high- and low-pressure phases. The third effect would produce such a mixture over a pressure range and could account for the observed effects.

Agreement of the transition pressure with previous work (*Introduction*) suggests that the observed effects are produced by the calcite-aragonite transition. The reversible nature of the transition, implied by the absence of aragonite upon terminal X-ray diffraction analysis (resolution 4 per cent), was confirmed by data obtained during pressure release (Figure 1).

At atmospheric pressure the density of aragonite is 9 per cent greater than calcite. If one assumes that the density increase due to the transition may be extrapolated downward (Figure 5), a 1.7 per cent density increase is obtained at atmospheric pressure. This suggests that only a fraction—roughly 20 per cent at 20 kb—of the calcite is transformed, probably due to effect (*c*) above, although effect (*a*) cannot be ruled out. Of course, this extrapolation relies upon the validity of using the ultrasonic data alone to obtain the pressure-density function

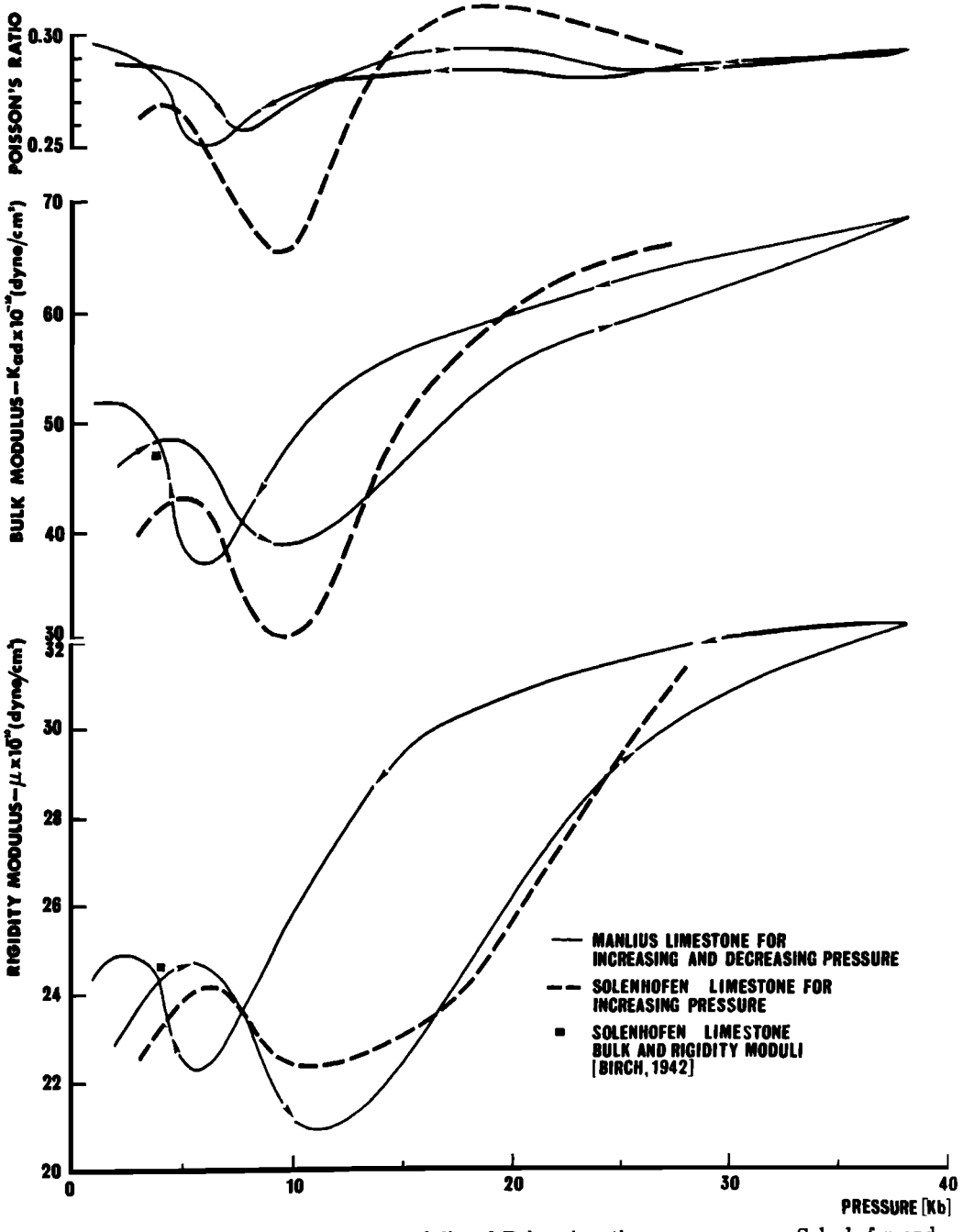

Fig. 9. Adiabatic bulk and rigidity moduli and Poisson's ratio versus pressure, Solenhofen and Manlius limestones.

(equation 3) as well as the assumption that the observed phenomena are due to a transition to aragonite rather than to another polymorph of different density. No clear evidence was found for the transitions statically observed by *Bridgman* [1939], *Jamieson* [1957, 1962], and *Adadurov et al.* [1961]. The variation in Poisson's ratio (Figure 9) above 20 kb, lying barely within the

uncertainty limits of the absolute value, is reproducible and may suggest further polymorphism.

The bulk and rigidity moduli decrease above the transition pressure and then gradually increase (Figure 9). A fraction of the decrease in bulk modulus—perhaps one-half—may be accounted for by the 15 per cent lower bulk modulus of aragonite as compared with calcite at atmospheric pressure. *Bridgman* [1949, p. 247] has demonstrated that it is not unusual for the high-pressure phase of a substance to have a greater initial compressibility than the low-pressure phase. With this decrease taken into account, there still remains a 15 per cent decrease in bulk modulus of the Solenhofen limestone on increasing pressure, and 3 and 18 per cent decrease for Manlius limestone on increasing and decreasing pressure. It is suggested that such a decrease in elastic moduli is characteristic of a transition in which both phases are present over a considerable pressure range. Although other transitions must be studied to establish this behavior as a general phenomenon, such a mechanism could account for at least a part of the observed decrease in seismic velocities at certain depths in the earth [e.g. *Gutenberg*, 1959, p. 81].

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